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VALENCE STATES OF SULFUR IN POLLUTION SAMPLES BY X-RAY ANALYSIS

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ABSTRACT

A flat single crystal spectrometer was configured to measure the valence band x-ray spectra of various forms of sulfur. While most different valence states showed differences in the structure of the Kβ band, particular emphasis was put on distinguishing sulfide from sulfate in samples simulating pollution particulate collections. The relative fraction of sulfide and sulfate in samples containing as low as 25 $\mu g/cm^2$ total sulfur can be measured with an accuracy of about 10%.

INTRODUCTION

The atomic number range from 11 (Na) to 17 (Cl) includes elements where the Kβ x-ray emission results from the transition of valence electrons (from the M shell) to fill a vacancy in the K shell. As such it displays structure associated with the chemical combination of the element. The chemical form of sulfur present in pollution samples is important in the data interpretation of the elemental analysis of such samples. The desirability of a routine method for identifying the valence state of the sulfur is clearly evident, particularly if it could be carried out concurrently with the elemental x-ray analysis.

This fine structure in the valence-band x-ray spectra has been studied for many years because it is a sensitive measure of chemical combination. Such measurements usually require the high resolution of a double crystal spectrometer.[1] By the choice of an appropriate crystal a single-crystal spectrometer can be configured so as to achieve resolution adequate to perform measurements of this type.

In this report we illustrate a particular configuration of a single-crystal, conventional x-ray fluorescence analyzer with the best practical resolution to measure the structure of the Kβ emission from various forms of sulfur. Further we demonstrate the ability to observe this structure in specimens containing sulfur at levels which are consistent with those which occur in many types of particulate pollution samples. But perhaps of the most importance, data are presented which show that, at total sulfur concentrations on the filter as low as $\sim$ 25 $\mu g/cm^2$, sulfate

and sulfide forms can be distinguished from one another, and their relative amounts determined with reasonable accuracy.

SUMMARY

A conventional wavelength-dispersion x-ray fluorescence spectrometer was used to identify and measure the sulfide and sulfate forms of sulfur at concentrations approximating pollution samples. It was necessary to substitute a NaCl crystal for the usual crystal in order to obtain enough resolution to distinguish the sulfide and sulfate features in the fine structure of the S Kβ line. Accuracy of the measurement of sulfide/sulfate ratio was demonstrated to be about 10%.

CONCLUSIONS

The results of the measurements reported here indicate that sulfur in air particulate samples can be identified as the sulfate or sulfide form; if both forms are present, their proportions can be determined quantitatively. Measurements made using a flat, single crystal, high resolution x-ray spectrometer are capable of about 10% accuracy in delineating the distribution between the two forms, at concentrations which might be expected in air particulate samples.

Extension of this technique to other elements is, of course, possible. The measurement of the valence state of P and Cl, immediate neighbors of S in the periodic table, should be analogous to what is reported here. Phosphorous has been studied[2] in a variety of compounds using a photographic Johann-type spectrograph; an application to chlorine has also been reported.[3] While the experimental details in these references differ from the technique reported here, the principles are the same.

On the other hand, the valence band transitions in some elements may require more specialized instrumentation. The L-lines of atomic numbers 24 to 30 (Cr to Cu), for instance, are low energy, less than 1 keV, and are difficult to measure at best. However, Henke and Taniguchi have shown[4] that it is possible to make measurements even as low in energy as 100 eV, using a more or less conventional single crystal spectrometer with a specially-designed low energy excitation source. The intermediate energy region (100 eV to 1-2 keV) can be directly attacked by such an approach.

RECOMMENDATIONS

This program was limited to the study of sulfide and sulfate forms of sulfur in pollution samples. The results indicate the potential of this technique. It is recommended that the technique be implemented for the examination of particulate pollution samples.

In order to carry out the implementation, the Naval Research Laboratory (NRL) has agreed to design and construct for the Environmental Protection Agency (EPA) a single crystal spectrometer channel for the multichannel x-ray analyzer presently in use at the EPA laboratories in Research Triangle Park, North Carolina. This component will be suited specifically to make the measurements appropriate to the determination of the valence state of sulfur during the period when the analyzer is performing the determination of the elemental composition of the sample.

In addition, NRL is presently constructing for EPA a compact x-ray sulfur analyzer intended for on-site use. Because of the success of the program to measure valence, this sulfur analyzer has been redesigned to enable it to perform the valence measurements as well as the analysis for total sulfur.

EXPERIMENTAL

EQUIPMENT

The single-crystal spectrometer used for this work is a standard x-ray fluorescence analyzer (Philips PW 1410). No modifications were necessary except to insure that the primary beam from the x-ray tube can be scattered into the spectrometer only by the sample itself; this is our standard configuration so that the background is minimized when analyzing "thin" samples. The instrument was operated manually although automated instruments of this type would be more efficient. Operating conditions are listed in Table 1.

Table 1. OPERATING CONDITIONS

X-ray tube:	Cr target; 45 kV, 45 mA.
Crystal:	Freshly cleaved (200) NaCl; 2d = 5.641 A.
Detector:	Gas flow proportional counter; 90% Ar, 10% CH_4 at atmospheric pressure; aluminized 6 μm Mylar window.
Collimator:	$\Delta\theta = 0.07^{\circ}$
Vacuum:	∿ 100 μm Hg

SAMPLE PREPARATION

Initially, bulk samples were prepared by loading plastic x-ray sample cups with reagent chemicals and closing the container with 6 μm mylar. Although the primary interest was in differentiating between sulfide and sulfate, other forms such

as elementary sulfur, sulfite and organic sulfur (thiourea) were prepared. The Kβ spectra of these bulk samples indicated significant differences in fine structure (as will be shown later) and suggested that micro-samples should be prepared.

Since the sulfide and sulfate compounds which were prepared in bulk were water soluble, the deposition of solutions on filter paper[5] seemed like a reasonable method of preparing micro-samples. Solutions of Na_2S and Na_2SO_4 were deposited on Whatman filter paper at concentrations such that the mass loading on the filter was approximately 50 μg of sulfur per square centimeter. X-ray measurements of these filters reproduced the spectra from the bulk samples of those compounds. Initially the mixtures of the sulfide and sulfate solutions were prepared at different ratios to produce intermediate samples having a total sulfur content of about 50 $\mu g/cm^2$. X-ray results were disappointing in that these mixtures seemed unstable; the spectra were not the mixture of the two forms as expected. Similarly, precipitating one of the forms of sulfur and depositing the other form as a solution onto the filter containing the precipitate did not produce adequate mixtures. In this case the solution deposited non-uniformly.

The method of preparation which produced satisfactory mixed samples in evaluating the proposed technique involved separate precipitation of each form of sulfur and sequential filtering onto Millipore. The sulfide was precipitated with a Cd^{++} solution and the sulfate with Ba^{++}. The use of relatively high atomic number cations has two beneficial effects: 1.) the samples effectively simulated actual collections where significant quantities of heavy elements may be present; and 2.) the Cd and Ba elemental concentration can be measured by x-ray fluorescence to confirm the sulfide-to-sulfate ratio present in the sample. One other type of sample was prepared at the 50-50 ratio: Filters containing pure end members of CdS and $BaSO_4$, at about 40 μg S/cm^2 each, were cut in half and reassembled between 6 μm Mylar sheets to form two mixed samples.

SPECTRA

Figure 1 shows the Kβ spectra from bulk samples. The different forms of sulfur can be distinguished from one another by the position of the main Kβ peak, the degree of asymmetry of this peak, and the presence or absence of peaks on the high or low angle side of the main peak. The most striking sifference occurs between the sulfide and sulfate where the sulfate is characterized by a high-angle secondary peak (commonly referred to as a satellite but more accurately described as a molecular orbital feature). The fine spectral features are in general agreement with those reported in a recent paper by Hurley and White,[6] who were concerned with measuring the chemical form of the sulfur in bulk samples of coal.

Figure 2 shows the Kβ spectrum from a mixed sample of precipitated material at a total sulfur content of 40 $\mu g/cm^2$ where approximately 50% of the sulfur is present as the sulfide and the balance as sulfate. The features used in the data interpretation are labelled "A" and "B".

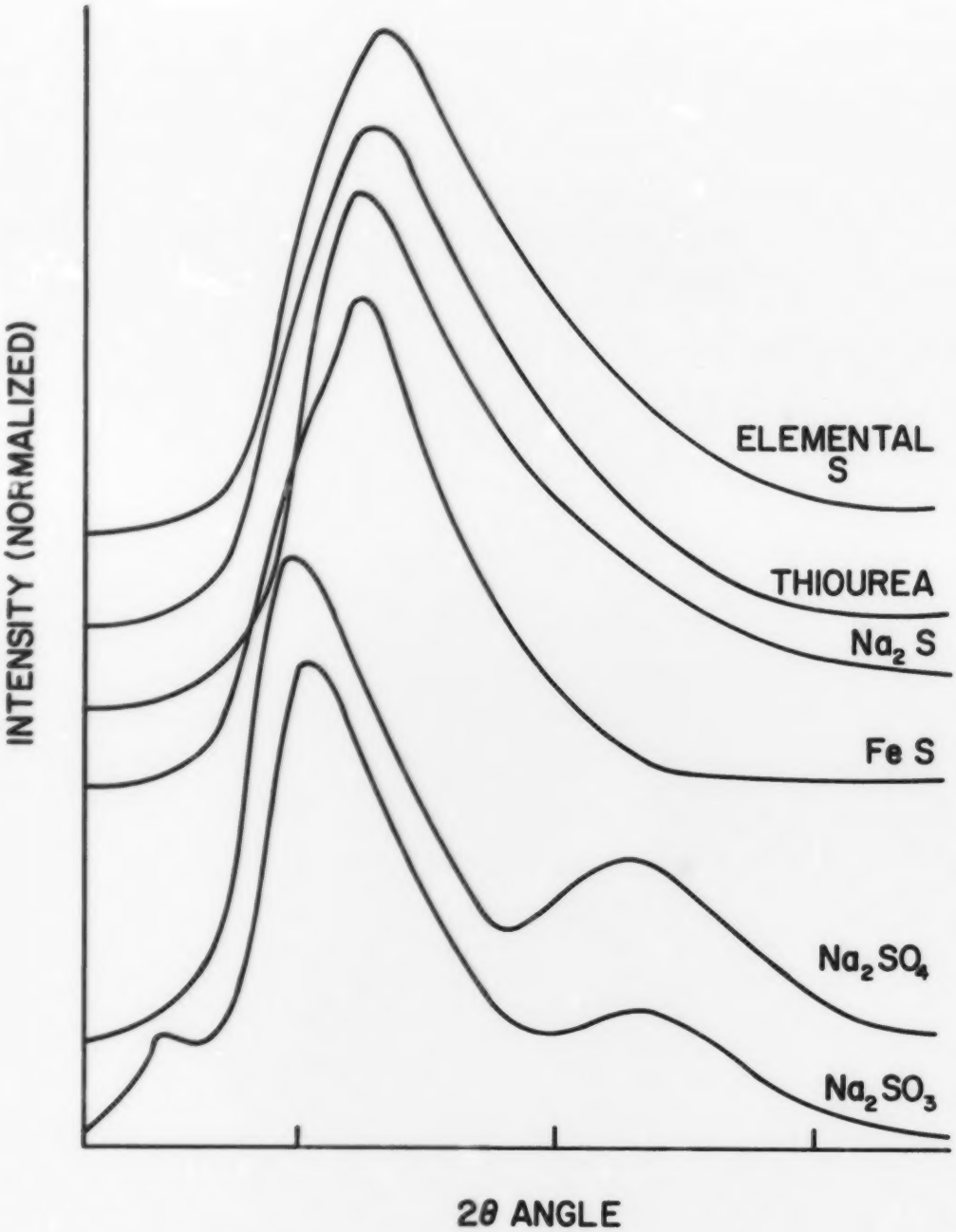

Figure 1. Kβ spectra of sulfur in various compounds. (The 2 eV bar is an estimate of the instrumental resolution with which the measurements were made).

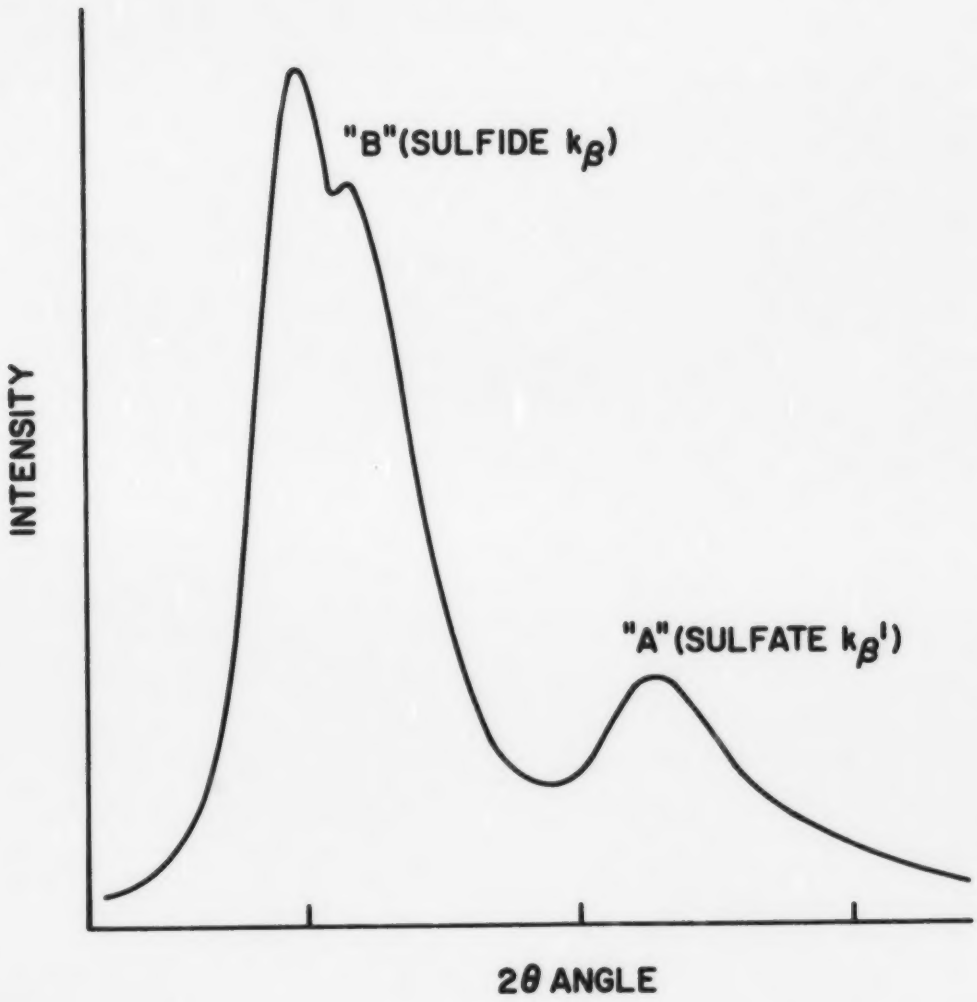

Figure 2. SKβ spectrum of 50% S as CdS, 50% S as $BaSO_4$.

CALIBRATION

CALCULATED CALIBRATION CURVE

A calibration curve for mixed samples can be calculated from measurements of separate sulfate and sulfide end-members. This calibration curve plots the ratio of Peak A to Peak B (from Figure 2) against the weight fraction of sulfur which is present as sulfide (or sulfate). For the pure sulfate A/B is 0.437; for pure sulfide it is 0.048. For mixed samples the ratio is simply

$$\frac{(C_{Sulfate})\ (A_{Pure\ Sulfate}) + (C_{Sulfide})\ (A_{Pure\ Sulfide})}{(C_{Sulfate})\ (B_{Pure\ Sulfate}) + (C_{Sulfide})\ (B_{Pure\ Sulfide})} \qquad (1)$$

where C = weight fraction

A = intensity measured at Peak Position A

B = intensity measured at Peak Position B.

A typical calculated calibration curve is shown in Figure 3, resulting from the calculation listed in Table 2, the end-number intensities being averaged from three sets of data. The curve is not linear because there is some intensity above background at each peak position from each of the forms of sulfur.

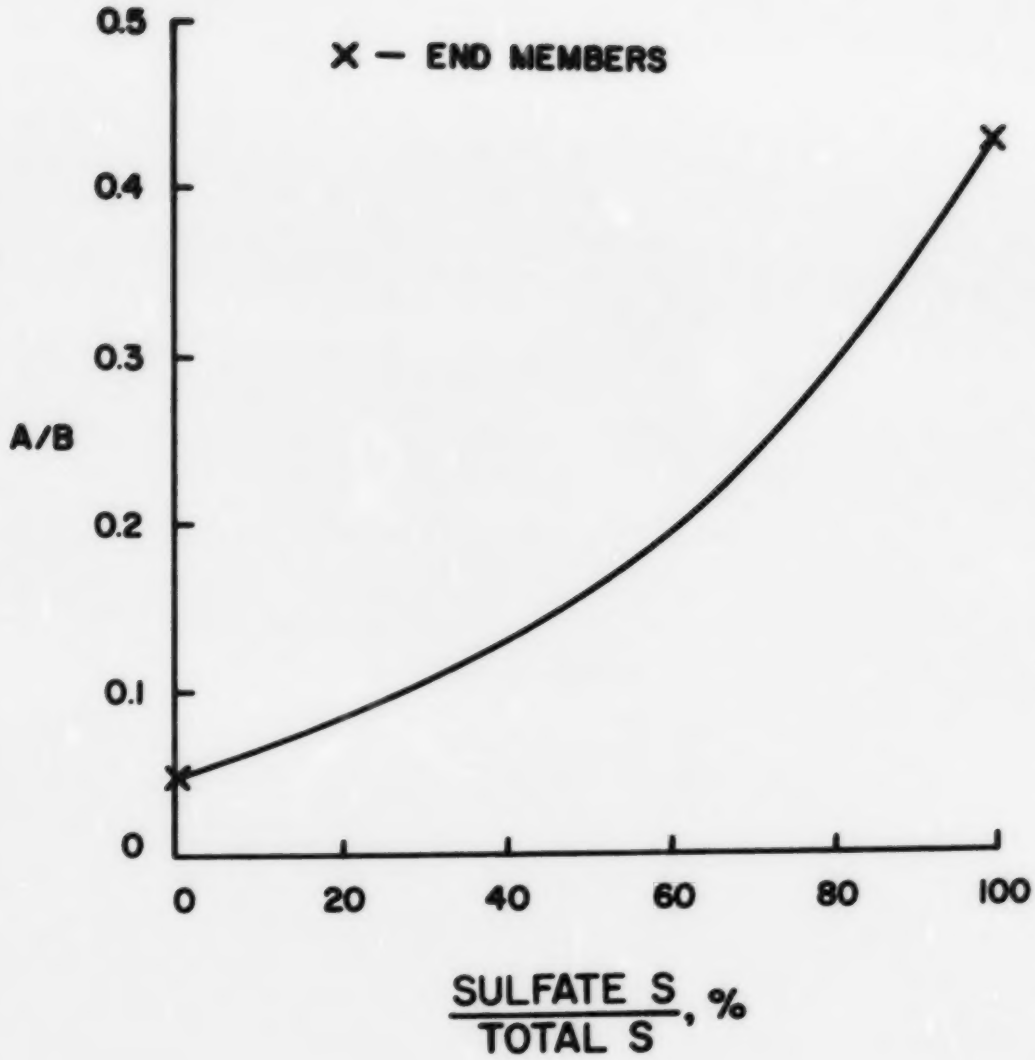

Figure 3. Calculated calibration curve.

Table 2. CALCULATION OF CALIBRATION CURVE

Distribution of Sulfur	Intensities (c/100 s) Sulfate Kβ′ Sulfide	Sulfate Kβ′ Sulfate	Sulfate Kβ′ Σ	Sulfide Kβ Sulfide	Sulfide Kβ Sulfate	Sulfide Kβ Σ	Ratio (Sulfate Kβ′/ Sulfide Kβ)
100% as CdS (Measured)	1651	0	1651	34286	0	34286	0.048
100% as $BaSO_4$ (Measured)	0	6412	6412	0	14681	14681	0.437
75% as CdS 25% as $BaSO_4$	1238	1603	2841	25714	3670	29384	0.097
50% as CdS 50% as $BaSO_4$	826	3206	4032	17143	7340	24483	0.165
25% as CdS 75% as $BaSO_4$	412	4809	5222	8572	11011	19583	0.267

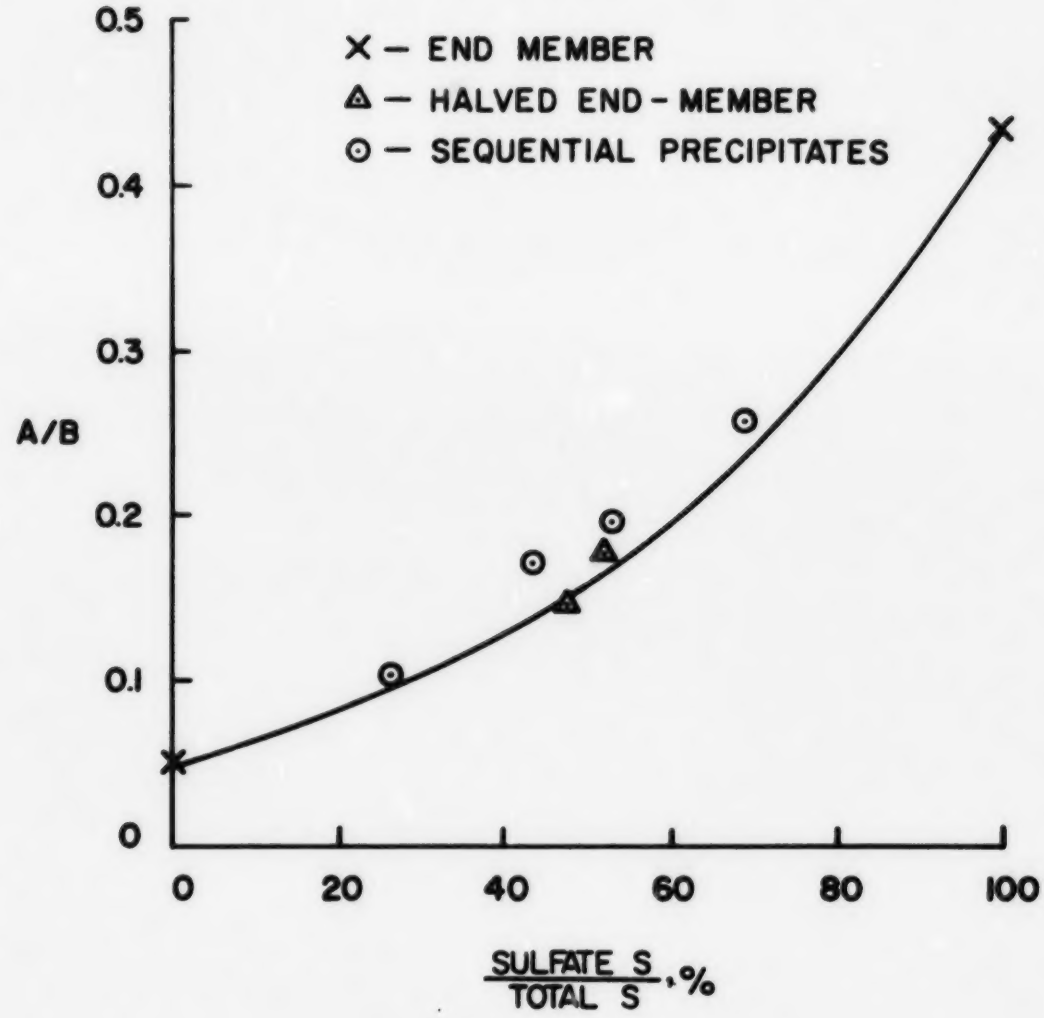

Figure 4. Intermediate composition measurements.

RESULTS AND DISCUSSION

The results of the measurements on the intermediate compositions are shown on Figure 4, the two different types of samples being distinguished by symbol. Table 3 lists the numerical results of the measurements obtained by using the calibration curve to convert the intensity ratios to percent sulfate. One would expect that the use of intensity ratios would make these measurements independent of the total sulfur content. A comparison of samples number 2 and 3 confirms this premise within the limits of this small range. Sample number 3, in fact, shows a more accurate result at 26 $\mu g/cm^2$ total sulfur than number 2 at 43 $\mu g/cm^2$ in spite of the calibration curve being prepared from end-numbers at the 40 $\mu g/cm^2$ level.

In the preparation of the sequentially filtered precipitates there was obvious non-uniformity on some filters; these samples were not used. Some of the uncertainty in the measurements undoubtedly arises from the non-uniformity in those samples where it was not obvious. The "halved end-member" samples (Nos. 5 and 6), which should not be plagued by this non-uniformity problem, give the best results of all. If the worst result (No. 2) is considered an outlier and dropped, the relative standard deviation (if meaningful for these few samples) improves from 11.5 to 7.5%.

Table 3. RESULTS FOR INTERMEDIATE COMPOSITION

Sample No.	Total S ($\mu g/cm^2$)	% of Total S[a]		% of Total S[b]		% Difference in measuring Sulfate
		as Sulfide	as Sulfate	as Sulfide	as Sulfate	
Sequentially Filtered Precipitates						
1	42	74	26	72.5	27.5	5.8
2	43	57	43	48	52	21
3	26	47	53	41	59	11
4	46	31	69	27	73	5.8
Halved End Members						
5	36	53	47	55	45	4.2
6	43	48	52	46	54	3.8
						R.S.D.= 11.5

[a]Based on XRF measurement for Cd and Ba.

[b]Based on A/B measurement and use of calibration curve in Figure 2.

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